Electrical activation and electrical properties of arsenic doped Hg$_{1-x}$Cd$_x$Te epilayers grown by MBE

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ABSTRACT

The annealing and electrical properties of extrinsic *in situ* doped mercury cadmium telluride (Hg$_{1-x}$Cd$_x$Te) epilayers grown by molecular beam epitaxy (MBE) on (211)B CdTe/Si and CdZnTe substrates are studied. The doping is performed with an elemental arsenic source. HgCdTe epilayers of CdTe mole fraction in the range of mid-wavelength infrared (MWIR) are grown at substrate temperatures of 175-185°C. The temperature dependent Hall effect characteristics of the grown samples are measured by the van der Pauw technique. A magnetic field of up to 0.8 T is used in these measurements. The analysis of the Hall coefficient in the temperature range of 40-300 K with a fitting based on a three-band non-parabolic Kane model, a fully ionized compensating donor concentration, and two independent discrete acceptor levels is reported. Both as-grown and annealed samples are used in this study. All of the as-grown samples showed *n*-type characteristics whereas annealed samples showed *p*-type characteristics. Activation annealing at different temperatures was performed. Conversion to *p*-type at lower than conventional annealing temperatures was achieved. Theoretical models are utilized to understand the dependence of the activated arsenic concentration on the annealing temperature.

Keywords: arsenic activation, annealing, molecular beam epitaxy, HgCdTe, van der Pauw, Kane model, Hall effect, MWIR.

1. INTRODUCTION

Hg$_{1-x}$Cd$_x$Te grown by Molecular Beam Epitaxy (MBE) has many important applications in infrared technology. Its bandgap tailorability, by changing x, the Cd mole fraction, permits one to tune to atmospheric transmission windows anywhere in the short wavelength infrared (SWIR) to the very long wavelength infrared (VLWIR) ranges. This can be achieved easily with MBE from run to run, or within a single run, with small calibration changes. In addition, an extra layer with a different x value can be used to filter out any unwanted portion of the incident spectrum.

Many state-of-the-art device structures require well-controlled *n*- and *p*-type doping with very well defined junctions. *N*-type doping of HgCdTe with indium is well understood and controllable down to concentrations in the mid-low 10^{14} cm^{-3}.[1] However, the *p*-type doping of HgCdTe is one of the few unsolved areas. *P*-type doping of HgCdTe with group-I elements gives very good Hall effect results with ~100% activation, but the high diffusivity of these elements[2,3] prevent them from being used in well defined junctions, as required for many devices. Group-V elements can be used to dope HgCdTe *p*-type if the doping species are made to occupy non-metal sites[4,5]. Among those group-V elements, arsenic is the most widely studied element for employment as a *p*-type dopant.
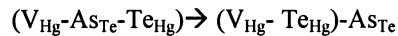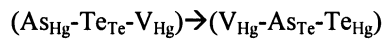
The p-type doping of HgCdTe can be achieved *ex situ* by either arsenic diffusion or ion implantation or *in situ* by direct alloy (conventional) doping or planar (delta) doping. There are drawbacks associated with each method. For example, arsenic diffusion does not permit one to control the profile and doping level, and the concentration decreases with increasing depth. Ion implantation introduces extensive structural damage and small electrical activity of arsenic. Also, the rate of evaporation, substrate orientation, and the sticking probability of arsenic

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determine its incorporation rate in HgCdTe. The sticking probability of arsenic is inversely proportional to substrate temperature. However, HgCdTe grown at a reduced substrate temperature results in lower crystalline quality material than when grown at a higher substrate temperature. Therefore one should keep a balance between the arsenic sticking coefficient and the crystalline quality of HgCdTe. Arsenic incorporation in HgCdTe does not depend on the Cd mole fraction, but it is inversely proportional to the Hg pressure in the chamber to a certain power (1-2).[6]

High structural and crystalline quality MBE growth of HgCdTe is restricted to the Te-saturated side of the existence region.[7] Growth away from the Te-saturated region results in strong twinning, which can be observed in Reflection High-Energy Electron Diffraction (RHEED) patterns. Arsenic doping of HgCdTe under Te-saturated conditions naturally results in most arsenic atoms occupying metal sites and hence behaving as donors rather than the desired acceptor character. When an elemental As source is used for doping, it is expected that the molecular flux from the arsenic cell will principally be in the form of As_4 molecules. A consensus exists that the As flux is in the form of tetramers,[8, 9] however there is an ongoing debate regarding the form in which arsenic incorporates into the material. Arsenic, by occupying both metal and non-metal sites and therefore giving both p- and n-type characteristics, strongly self-compensates. As-grown samples usually show slightly n-type characteristics[10,11]. For As concentrations higher than 2×10^{18} cm^{-3}, the activation ratio rapidly falls off due to the decreasing solubility of arsenic[12] in HgCdTe.

There are many possible reactions for As to travel from a metal site to an non-metal site, and hence become an acceptor.[6] One possible reaction proposes that the Hg vacancy (V_{Hg}) plays an important role in transferring As to the non-metal site;[5]

$$(As_{Hg}\text{-}Te_{Te}\text{-}V_{Hg}) \rightarrow (V_{Hg}\text{-}As_{Te}\text{-}Te_{Hg})$$

$$(V_{Hg}\text{-}As_{Te}\text{-}Te_{Hg}) \rightarrow (V_{Hg}\text{-} Te_{Hg})\text{-}As_{Te}$$

V_{Hg} will act as a catalyst; hence its number density should be preserved until the site transfer is complete. The density of V_{Hg}-Te_{Hg} complexes will then become saturated and they will diffuse to the surface of the HgCdTe epilayer, leaving behind As atoms occupying non-metal sites.

2. EXPERIMENTAL

$Hg_{1-x}Cd_xTe$ layers for annealing studies and electrical characterization with x values in the MWIR ($x \sim 0.3$) region were grown in a RIBER3200 MBE chamber. Substrate preparation prior to growth is described in detail elsewhere.[10] The growth of the HgCdTe layers was done under Te saturated conditions. Close monitoring of the RHEED patterns indicated 2D growth. All layers studied here were grown at the rate of approximately 2μm/h, had a final thickness of 4-5 μm, and were doped with the conventional method. HgCdTe growth was terminated by growing a protective CdTe layer of 0.3-0.4 μm thickness. The cut-off wavelengths were measured at room temperature using a Fourier transform infrared (FTIR) spectrometer to extract x values and the thickness of the HgCdTe layers. X-ray rocking curves were also measured to check the crystalline quality. The cap layer was wet etched before the Hall effect measurements. Hall effect measurements on both as-grown and annealed samples were performed with the van der Pauw technique. The temperature range was 40-300K and magnetic field strengths of up to 0.8 T were employed.

The activation annealing of four As doped samples was done with a closed tube two-zone annealing system. A description of the annealing apparatus and experimental details has been published elsewhere.[10] The annealing of arsenic doped samples is performed by first keeping the Hg zone temperature lower than the sample zone to create extra Hg vacancies, which is followed by an isothermal anneal. Figure 1 shows schematically the Hg zone temperature T_1 (Zone1) and the sample zone (Zone2) temperature T_2 versus time. T_3, the final isothermal anneal temperature, is usually chosen to be equal to T_2. A list of the studied temperatures and annealing times is shown in Table 1. We also, for comparison, skip the first step to compare the effect of a lower Hg temperature on the activation of arsenic (set 5 and set 6). We have also kept the annealing time longer for some samples to see the change in activation with time (set 4 and set 7). For sets 1 and 5, the temperature ramp between the first temperature step and the second temperature step was completed in 30 minutes, and the second ramp was 20 minutes. For sets 2, 3, 4, and 8, the ramp between the first temperature step and the second temperature step was 20 minutes. Set 6 maintained a single isothermal temperature in comparison with set 2. For set 7, the ramp was 10 min.
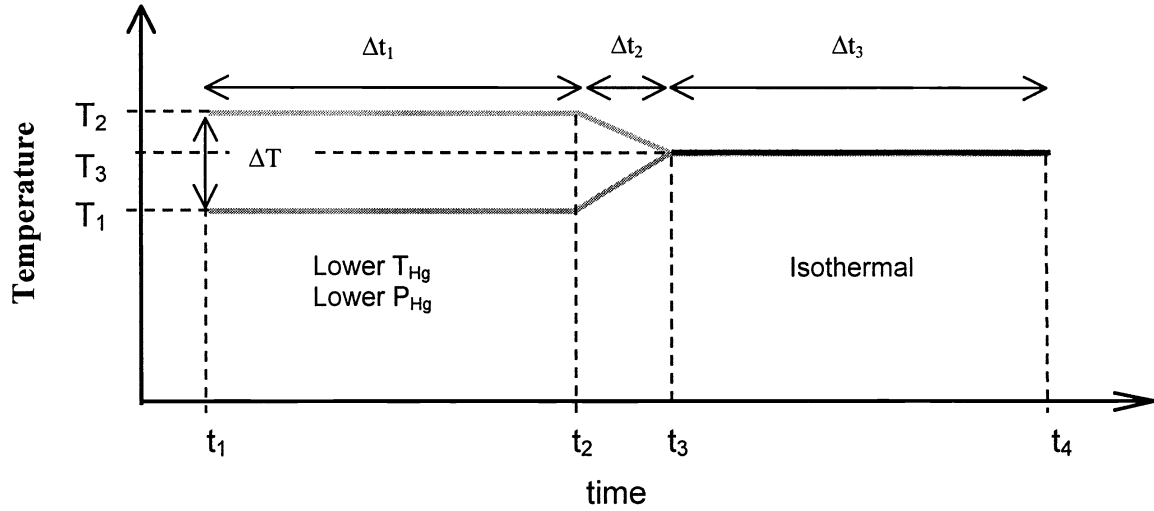
Figure 1 schematic labels:

Temperature axis: T_2, T_3, T_1, ΔT

Δt_1, Δt_2, Δt_3

Lower T_{Hg}
Lower P_{Hg}

Isothermal

time axis: t_1, t_2, t_3, t_4

Figure 1. Schematic of annealing temperature versus time. T_1 is Hg zone temperature (Zone1), T_2 is sample zone temperature (Zone2). T_3 is the final isothermal temperature (Zone1 and Zone2) and usually equal to T_2.

Table 1. Temperature (°C) and time settings for arsenic activation annealing of HgCdTe samples

Set	Zone1	Zone2	time	Set	Zone1	Zone2	time
1	422 297 232	425 300 235	15min 12h 12h	5	450 300 250	450 300 250	15min 12h 12h
2	250 300	300 300	12h 12h	6	300	300	24h
3	200 250	250 250	12h 12h	7	250 275	275 275	13h 28h
4	200 250	250 250	24h 40h	8	225 275	275 275	12h 12h

We also studied the electrical properties of the in situ As doped HgCdTe epilayers. The Hall coefficient obtained from temperature dependent Hall effect measurements for these layers are fitted with a fitting program using a three-band Kane model with three dopant levels. The fitting gives information regarding the concentration of the acceptor and donor species and their activation energies.

3. RESULTS AND DISCUSION

Typical plots of carrier concentration and mobility versus reciprocal temperature with different annealing temperatures are shown in Figures 2a and 2b, respectively. All as-grown samples were found to exhibit n-type characteristics. We achieved p-type conversion of these layers after the various anneals (Table 1). As seen from Figure 2 (a), as the isothermal annealing temperature is increased, the activation of As is more effective (up triangles and circles). This is also true for increased annealing times for the lower Hg zone isothermal annealing combinations (diamonds and down triangles). In Figure 3, we plot one of the sample's p-type conversion after long and short annealing times at the same temperature setting. N-type to p-type conversion shows a very sharp peak for the longer annealing time. For the shorter annealing time, the conversion is at a lower temperature, giving the suggestion that the arsenic concentration on metal sites (p) is lower than that on non-metal sites (n) compare to the longer annealing time (see equation (2)).
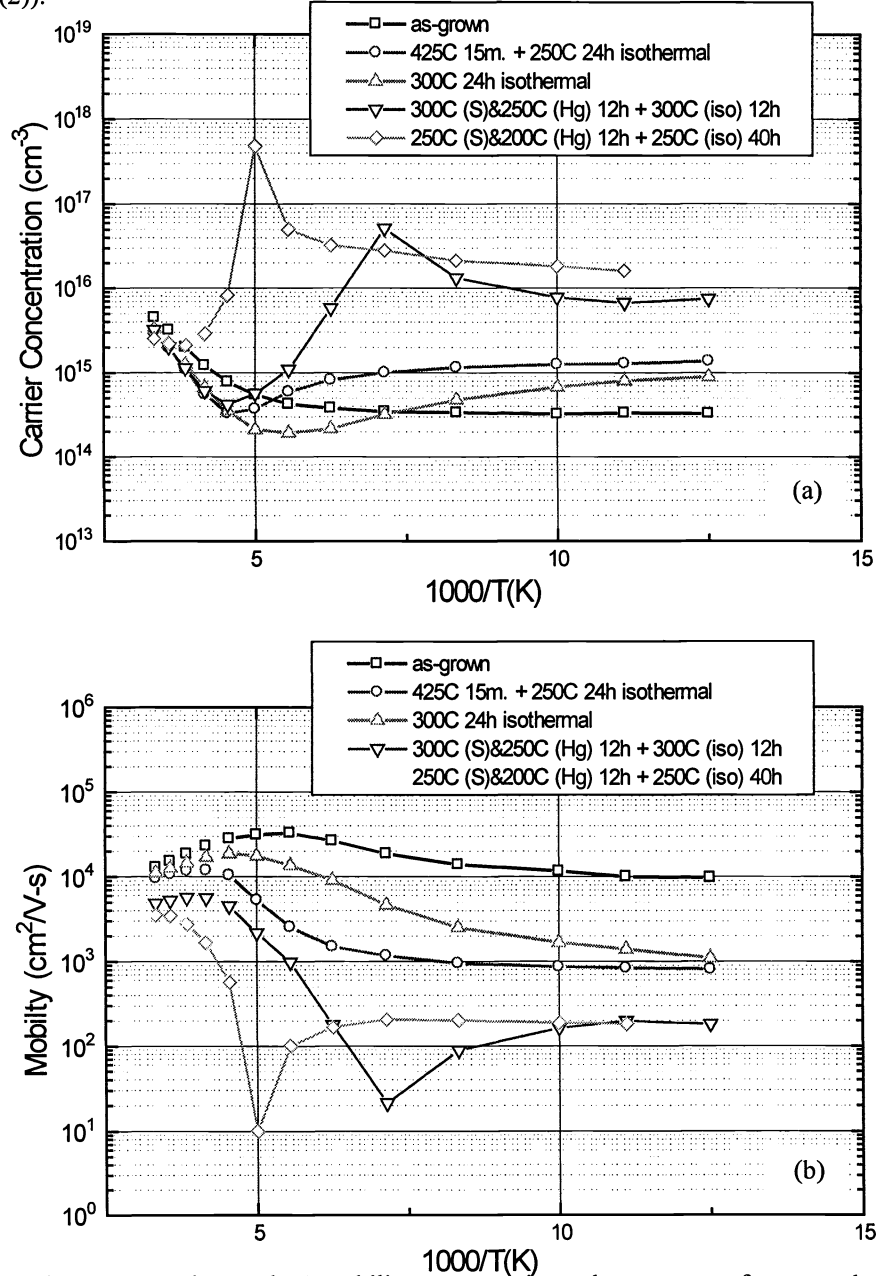

Figure 2. (a) Carrier concentration, and **(b)** mobility versus reciprocal temperature for a sample annealed at different temperatures.
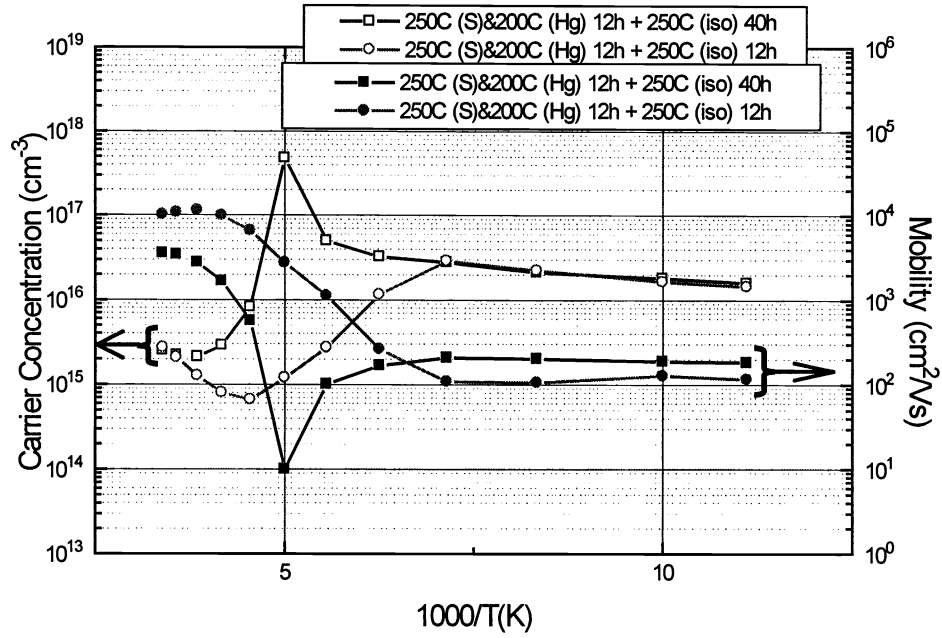
Figure 3. Carrier concentration and mobility versus reciprocal temperature for a sample annealed at the same temperature settings but different annealing times.

P-type doped HgCdTe will not only have acceptor species, but will typically also have other impurities acting as acceptors and donors. There are many electrically active defects, including vacancies, intersitials and impurity species, that may give p- or n-type characteristics. V_{Hg} is a very well known defect that acts as an acceptor. In fact, most p-type HgCdTe layers are achieved by vacancy doping due to the p-type dopant problems that this paper addresses. There will also be impurities showing n-type characteristics. Note that as-grown As doped HgCdTe layers usually show n-type characteristics[10]. This may be a consequence of the Te-saturated growth conditions forcing some arsenic atoms to occupy metal sites where they act as donors, or may be due to background impurities. When both holes and electrons are present in an epilayer, the Hall coefficient must be calculated in the form [13]

$$R_H = \frac{(p - b^2 n) + (\mu_n B)^2 (p - n)}{q[(p + bn)^2 + (\mu_n B)^2 (p - n)^2]}, \tag{1}$$

where b is the donor to acceptor mobility ratio, μ_n / μ_p, B is magnetic field strength, and p and n are the acceptor and donor concentrations, respectively. For sufficiently low magnetic fields, $B \ll 1/\mu_n$, and $p \gg n$, equation (1) can be replaced by

$$R_H \approx \frac{(p - b^2 n)}{q(p + bn)^2}. \tag{2}$$

The carrier concentration vs. 1000/T data points obtained from Hall effect measurements are values averaged over the grown layer. Therefore, a direct extrapolation of the data points to find the ionization energies of impurity levels will usually not give accurate results. For this reason, a fitting program using a Kane model with non-parabolic bands has been developed at the Microphysics Laboratory (MPL). The program also assumes two acceptor levels and a single donor level for fitting. The fitting was done to the Hall coefficient, given by equation (2). The low magnetic field assumption is very well justified, since the carrier concentration and mobility versus reciprocal temperature show very little dependence on magnetic fields up to 0.8 T (see Figure 1 of reference 10). It has been determined experimentally that the exponent of the mobility ratio is not exactly equal to but close to 2. The program

does not assume the mobility ratio exponent is equal to 2, but rather treats it as another fitting parameter. Therefore equation (2) is replaced with the very similar one,

$$R_H = \frac{(p - b^c n)}{q(p + bn)^2}.$$ (3)

CdTe/Si substrates have advantages over CdZnTe substrates in terms of cost and physical durability. From fittings of Hall effect results, we found no clear distinction between CdZnTe substrates and the CdTe/Si substrate of this study. This could be good news for CdTe/Si substrates, but is subject to more detailed study.

After post-growth annealing, the samples converted to p-type, as shown in Figures 2. The conversion process may be complex since arsenic does not necessarily incorporate into HgCdTe as single arsenic atoms, as has been previously assumed. Theoretical work at MPL has concluded that there is evidence that arsenic may be incorporated as tetramers (As_4), or As_4 clusters for As_4 sources. Calculations using the general principles of quasithermodynamic theory, employing the law of mass action to calculate the relations between the arsenic concentration and the arsenic and Hg partial pressures led to this conclusion.[6, 11] The conversion to p-type behavior may occur by the breakup of tetramers resulting in arsenic atoms occupying Te sites.[8, 11] As seen from Figure 2 (a), the increase in the doping level ($|N_d-N_a|$) would then be due to the transfer of some arsenic atoms to Te sites, upon which they start to act as acceptors.

The lower mobility of as-grown layers, showing n-type characteristics, compared to indium doped n-type layers with the same doping levels, is attributed to the presence of additional strong scattering centers, such as As_4 and its clusters. Table 2 shows a summary of the fitted Hall effect results. The shallow and deep levels found by fitting to Hall effect data are compared to the HgCdTe energy gap calculated by [14]

$$E_g(x, T) = -0.302 + 1.93x - 0.81x^2 + 0.832x^3 + 0.000535T(1 - 2x)$$ (4)

for x values between 0.2 and 0.4 at 80 K. In this fitting study, shallow level energies due to arsenic impurities were lower than 10meV for x < 0.36. Deep levels, which were assumed to be V_{Hg}, were close to the intrinsic level with most of the points in the 60-110 meV range. After annealing, a very low V_{Hg} concentration is observed due to isothermal annealing filling those vacancies.

Table 2. Fitting of Hall effect results of arsenic doped samples with various Cd mole fractions.

Sample	x (%)	$N_d(cm^{-3})$ x10^{16} Donor Conc.	$N_{a1}(cm^{-3})$ x10^{16} As Conc.	$N_{a2}(cm^{-3})$ x10^{16} V_{Hg} Conc.	E_{a1} (meV) As Ionization Energy	E_{a2} (meV) V_{Hg} Ionization Energy
1	36.5	1.5	3.3	0.011	10.2	107.6
2	35.0	0.82	27.0	0.0026	5.6	108.8
3	29.9	0.001	27.02	0.001	4.2	101.0
4	29.1	1.02	4.22	0.01	3.7	84.0
5	28.9	5.9	11.0	0.00098	7.7	152.1
6	26.9	6.73	15.01	0.48	3.5	32.6
7	25.4	0.033	4.3	0.0002	6.0	99.9
8	23.3	7.5	21.0	0.001	3.2	59.6

4. CONCLUSIONS

We have studied *p*-type activation of As doped HgCdTe epilayers grown by MBE. As-grown arsenic doped layers grown under Te saturated conditions were *n*-type, as expected. The activation of As was achieved at the lower temperatures than conventional *p*-type annealing temperatures. Two zone annealing with a lower Hg pressure annealing followed by isothermal annealing was successfully used to obtain an *n*-type to *p*-type conversion. We have determined the annealing temperatures and annealing times required for the activation of As in HgCdTe. We have studied Hall effect data of arsenic doped HgCdTe layers in greater detail. We obtained, from fitting the Hall effect results, very shallow levels for arsenic with ionization energies lower than 10meV. Deep levels are very close to the mid-gap, with ionization energies principally in the 60-110meV range. The concentrations of these mid-gap levels must be reduced in order to improve the device characteristics of the HgCdTe layers.

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